IN-LINE DIELECTRIC MONITORING DURING EXTRUSION OF FILLED POLYMERS

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Abstract

Dielectric measurements were made on clay filled polyethylene-ethyl vinyl acetate (EVA) copolymer nanocomposites during processing by extrusion. The results show that, at processing temperatures, composites containing chemically treated clays display significant dielectric dispersions. The addition of natural clay to the EVA copolymer increased the dielectric constant (relative permittivity) above that of the EVA copolymer but did not increase the conductivity or cause any dispersion. The chemically treated clays, which are known to exfoliate when compounded with EVA copolymer, gave substantially higher relative permitivity and conductivity having distinct variations with frequency consistent with dielectric relaxations at frequencies below 3000 Hz. One clay treatment gave a larger dielectric dispersion than the other.

Introduction

Mineral fillers are added to polymers to produce compounds with enhanced physical properties. Typical particle sizes are greater than 10^{-6} m and loadings are up to 30% and higher. Recently introduced nanocomposite materials employ fillers with much smaller sizes, of order 10^{-9} m, that exfoliate under the correct, and often difficult to achieve, conditions to yield superior physical properties at much lower loading levels (3 – 5 wt.%). They reportedly offer excellent flame-retardant properties.

Producers of nanocomposite materials must control both the concentration of filler and the extent of exfoliation to maintain the quality of their products.

In-line dielectric sensors [1] have been successfully used to quantitatively measure in real time concentrations of fillers, additives, solvents and gases in polymers, compounds and other materials. Dielectric analyzers are among the few in-line instruments that can measure chemical concentrations in opaque as well as transparent liquids. This work suggests that in-line dielectric spectrometers might also monitor exfoliation in nanocomposites during processing.

Theory

When a material, for example a polymer melt, is subjected to an electrical field, bound charges are displaced and dipoles are oriented. The extent of this displacement is characterized by the relative permittivity ε of the material. In non-polar materials, displacement is due to electrons that polarize quickly and ε is substantially independent of frequency, additive by molecular groups and capable via mixing rules of yielding quantitative concentration determinations. In polar or inhomogeneous materials, larger slower structures or interfaces can polarize in applied electric fields. They contribute to ε only if the frequency of the applied field is low enough. As the frequency of the applied field increases in these materials, fewer of the dipoles can orient (relax) quickly enough to keep up or less charge accumulates at the interfaces, and ε decreases. Conductivity σ can include a frequency independent component σ_{DC} associated with the drift of unbound charges and also a frequency dependent component σ_r related to dielectric relaxation [2].

$$\sigma = \sigma_{DC} + \sigma_r \qquad (1)$$

The relaxation part ε_r'' of the dielectric loss factor is defined as

$$\varepsilon_r'' = \frac{\sigma_r}{\omega \varepsilon_0} \qquad (2)$$

where $\omega = 2\pi *$ frequency and $\varepsilon_0 = 8.854 * 10^{-12}$ F/m. In cases where dipolar motions have a single characteristic relaxation time, plots of ε'' vs ε' describe semicircular arcs. In materials with dipoles of different sizes, there is a distribution of relaxation times and the arcs are skewed.

Equipment

To an 18 mm diameter Haake twin screw extruder was bolted a 25 mm thick adapter plate with a conical interior that tapered down to 12 mm ID. Installed next in-line was a housing that contained a dielectric sensor, a 12 mm ID by 25 mm long ceramic ring [Figure 1]. Resin flows inside the ring and experiences electric fields from interdigitated electrodes (0.33 mm spacing) on the sensor's inner surface. Weak electric field lines fringe about a millimeter into the processed materials. Beyond the sensor housing was a 12 mm ID die piece 25 mm

long. Assembly to the extruder was accomplished using bolts that were inserted through the die plate and sensor housing and tightened into threaded holes in the adapter plate at the exit of the extruder. The dielectric sensor assembly was temperature controlled and included melt temperature and pressure transducers.

The sensor's capacitance C and resistance R are given by

$$C = \boldsymbol{e}_0 g\left(\boldsymbol{e} + \boldsymbol{e}_{cer}\right) \tag{3}$$

$$\frac{1}{R} = g\left(\boldsymbol{s} + \boldsymbol{s}_{cer}\right) \tag{4}$$

where g is a geometrical constant (units meters) characterizing the sensitivity of the sensor and ε_{cer} and σ_{cer} are the relative permittivity and conductivity of the ceramic material of which the sensor body is constructed. The calibration quantities ε_{cer} and σ_{cer} depend on temperature and frequency while g is a constant. Electronic instrumentation applies sinusoidal voltages (amplitude programmable, set at 1.0 V_{rms}) to the sensor electrodes and measures the resulting current and phase angle to determine C and R. It then uses Equations (3) and (4) to determine the ε and σ of the process fluids at sixteen point frequencies between 500 Hz and 100,000 Hz in continually repeating sweeps that took about two minutes each. The present equipment can measure at lower frequencies (down to 10^{-3} Hz) but it takes more time. Data is automatically archived in a database with time stamps.

Standarad uncertainties for the measurements were 1 °C for temperature and 70 kPa (10 psi) for pressure. Uncertainty in the electrical measurements is discussed below.

EVA copolymer was Equistar UE630-000 with 17% vinyl acetate. Clays were Southern Clay Products natural, Cloisite 15A and 30B nanoparticles of alkyl-quaternary ammonium montmorillonite.[3] Clay samples were dried at 100 °C under vacuum for at least an hour before use. Pax-purge was from Paxton Polymer Co.[a]

Procedures

On a test stand at a temperature of 35 °C, measuring C when the sensor was empty, i.e. filled with air, and then measuring again when it was filled with a reference solvent of known permittivity determined g. After this, with g entered in the software and the sensor empty, ε_{cer} and σ_{cer} were determined at each frequency at temperatures of 35, 97, 177 and 222 °C to establish the calibration. During subsequent operation ε_{cer} and σ_{cer}

were determined at the measured operating temperature by linear interpolation between the nearest calibration temperatures.

On Day 1 of these experiments, the system was heated to 150 °C and measurements were taken in air. Then unfilled EVA copolymer was extruded at 40 revolution / minute. Small batches of 4.7% mass fraction of natural clay in EVA (5 grams clay per 100 grams polymer) were frequently mixed by manual weighing and added to the extruder when the hopper ran nearly empty. The weight fraction of clay was controlled to within 0.2%. After the natural clay compound thoroughly pushed out the unfilled EVA and stable measurements were obtained, the type of clay was changed to 30B. Again, extrusion was continued until the measured values stopped changing. Extruding unfilled EVA, Pax-purge and then more EVA cleaned the extruder. On Day 2, unfilled EVA was extruded at 150 °C again to confirm consistency with the previous day's readings. Then, 15A clay compound was extruded for the final data set.

Results

Figures 2 and 3 show ε and σ at all the measurement frequencies versus time for the Day 1 tests. ε of the unfilled EVA copolymer melt at 150 °C measured 2.33 at 500 Hz. This is consistent with the prediction of additive group calculations [4]. Natural clay was added, and this caused ε to increase gradually with no dispersion (variation in ε with frequency) or increase in σ. Clay coated with 30B exfoliating treatment was added and again ε increased, but this time ε showed a small amount of dispersion and σ increased. Figures 4 and 5 show ε and σ at all the measurement frequencies versus time for the Day 2 tests. On Day 2 the readings with unfilled EVA were indistinguishable from the readings on the same material the previous day. Clay coated with 15A exfoliating treatment was added and this time ε and σ increased dramatically and a large dispersion appeared.

Analysis

Uncertainties in the electrical measurements were negligible compared to the systematic errors that were readily quantified by comparing empty sensor readings at the start of tests to the known electrical properties of air ($\varepsilon_{air} = 1.00$ and $\sigma_{air} = 1.5e-12$ S/m). The discrepancies represented the accumulated systematic errors and are shown in Figures 2, 3, 6 and 7. They were worst at 10^5 Hz where they were 0.2 for ε and 4e-7 S/m for σ. At 500 Hz they were 0.04 for ε and 2e-9 S/m for σ. The combined uncertainties and systematic errors were small enough to clearly identify differences between the materials. Two possible causes of the systematic errors

were: a.) The tests were run at 150 °C but the nearest calibrations were at 97 and 177 °C; and b.) On a previous day nylon 6 was measured. The sensor was cleaned but some residual contamination may have remained. Systematic errors determined from empty sensor readings could be reliably removed by subtraction if they originated in the temperature calibration, but not if they originated from contamination. At 10^5 Hz, ε_{cer} was 9.82 at 97 °C and 9.93 at 177 °C. The difference, 0.11, represents the largest possible error contribution from the temperature dependence of calibration at that frequency. Since the empty sensor readings at 10^5 Hz showed approximately twice this amount of systematic error, some other cause, possibly contamination, must have contributed. Therefore, no subtractions were made.

The transition time, i.e. the time it takes for one material to thoroughly push out another and for the readings to stabilize to their new values, was about two hours with these EVA compounds at these processing conditions. In previous work [5] at different processing conditions with unfilled EVA copolymers and a larger (45 mm compared to 12 mm ID) dielectric sensor having wider electrode spacing (1.3 mm compared to 0.33 mm), transitions were faster by a factor of about four (around 30 minutes). Coincidentally, this factor is about the same as the ratio of the electrode spacings of the two sensors. The closer the electrode spacing, the more shallow the penetration of the electric fields into the melt and the more thoroughly one material must push out another during transitions for the material in the majority of the measurement volume to be displaced. Therefore it is reasonable that transitions are slower for sensors with closer electrode spacing. Subsequent experiments with nylon using the small sensor showed much faster – usually less than 15 minutes or more than eight times faster – transitions than with EVA at roughly the same processing conditions. Faster transitions in nylon than in ethylene polymers have been reported before [1] with the large sensor. Possible causes for this difference could include the lower viscosity or the higher surface energy of the nylon resins.

Figures 6 and 7 show the ε and σ readings versus frequency for each of the materials, including air with the empty sensor just before the tests. Figure 8 shows plots of loss factor versus ε for the two nanocomposites prepared with exfoliating treatments.

The data clearly showed that: a.) EVA and EVA with 4.7 % natural clay had σ about the same as air; b.) EVA elevated ε uniformly at all frequencies, and EVA with natural clay elevated it further, but neither of these materials caused any noticeable dispersion; and c.) EVA with the treated clays had higher ε, σ and dispersion, more so with the 15A treatment than with the 30B treatment.

With the 15A exfoliating treatment the relaxation is much larger than with the 30B treatment.

Conclusions

EVA / clay nanocomposites prepared with exfoliating treatments had dielectric relaxations during extrusion. Treatment 15A gave a large relaxation. Treatment 30B gave a very small relaxation. Nanocomposites prepared with the same amount of untreated clay and unfilled EVA gave no relaxation. Additional chemical and physical characterization of the samples and more experiments are needed to confirm it, but this data suggests an association between exfoliation and dielectric relaxation.

[a] Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

References

[1] M. McBrearty, A. Bur, S. Roth, SPE ANTEC Conference Proceedings, 2000, p. 287 – 291.
[2] J. Runt & J. Fitzgerald, *'Dielectric Spectroscopy of Polymeric Materials'*, American Chemical Society, Washington DC, 1997
[3] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, and D. R. Paul Proc. SPE Ann. Tech. Mtg. May, 2000.
[4] D. W. Van Krevelin, *'Properties of Polymers'*, Elsevier, Amserdam, 1990
[5] S. Perusich, M. McBrearty, Polymer Engineering & Science, Jan 2000, Vol. 40, No. 1, pp. 214 – 226.

Figure 1. In-line dielectric sensor. 12 mm ID, 25 mm length. Material flows through hole in center. Interdigitated electrodes 0.33 mm spacing on inner surface. Contacts on upstream and downsteam faces.
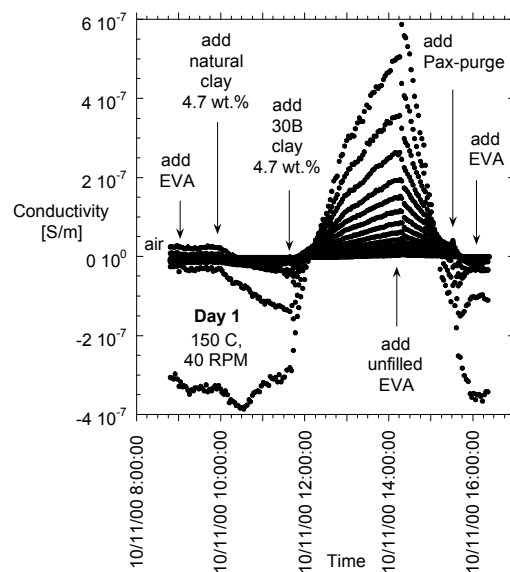

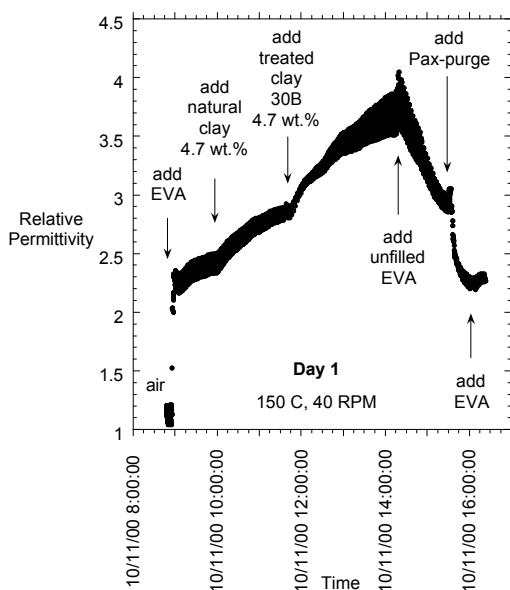Figure 3. Conductivity σ versus time, day 1. Frequencies 500 Hz to 10^5 Hz.

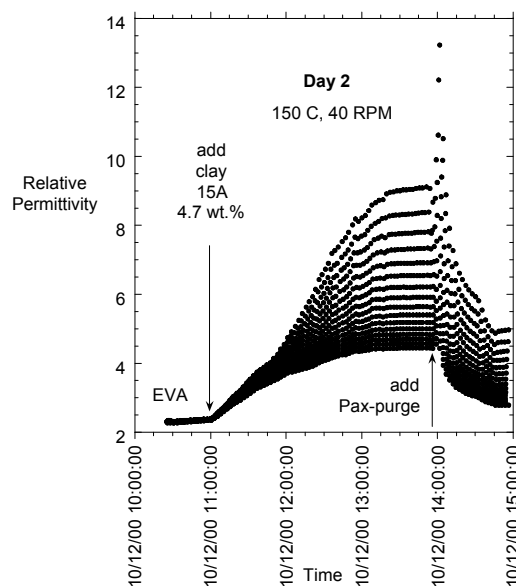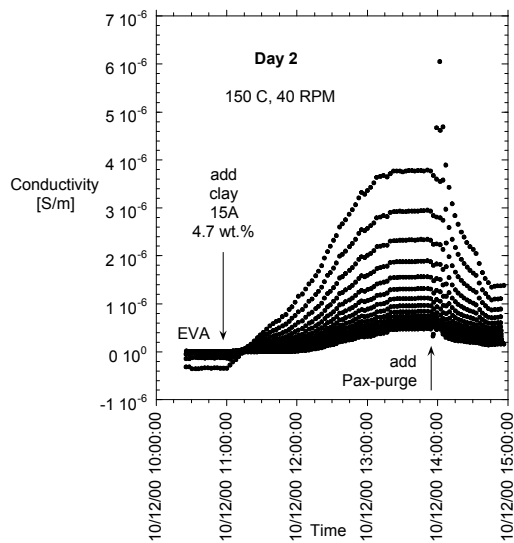Figure 2. Relative permittivity ε versus time, day 1. Frequencies 500 Hz to 10^5 Hz.

Figure 4. Relative permittivity ε versus time, day 2. Frequencies 500 Hz to 10^5 Hz.

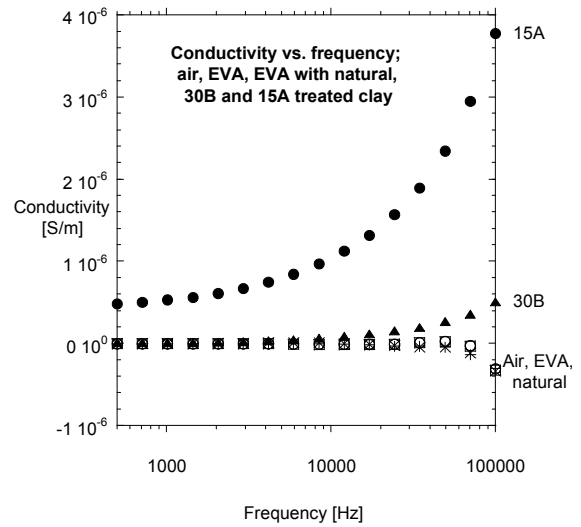Figure 5. Conductivity σ versus time, day 2. Frequencies 500 Hz to 10^5 Hz.

Figure 7. Conductivity versus frequency; air, EVA, EVA with natural clay and EVA with treated clays 30B and 15A.
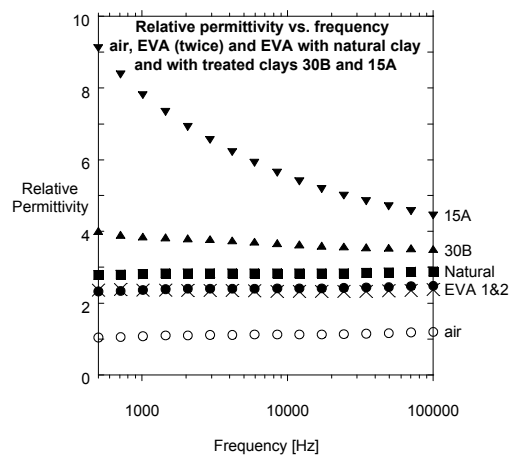

Figure 6. Relative permittivity versus frequency; air, EVA, EVA with natural clay and EVA with treated clays 30B and 15A.
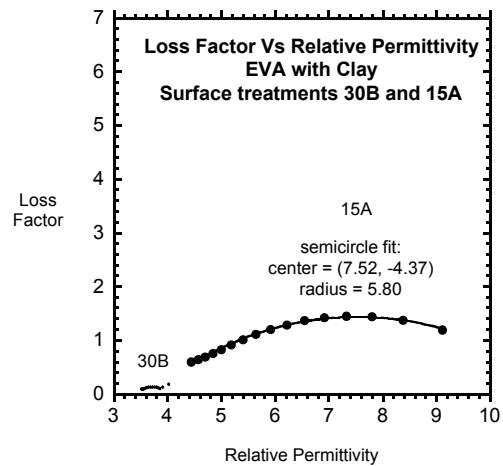

Figure 8. Loss factor vs. permittivity, EVA with treated clays 30B and 15A.